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U. S. DEPARTMENT OF AGRICULTURE.

OFFICE OF PUBLIC ROADS—BULLETIN No. 30.

LOGAN WALLER PAGE, DIRECTOR.

THE CORROSION OF IRON.

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BY

ALLERTON S. CUSHMAN,

ASSISTANT DIRECTOR, OFFICE OF PUBLIC ROADS.



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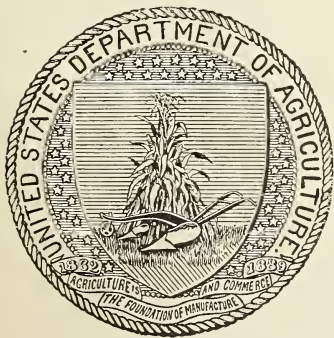
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THE CORROSION OF IRON.

INTRODUCTION.

In 1905 the Department of Agriculture published Farmers' Bulletin No. 239 on the subject of corrosion of fence wire. A large number of complaints had reached the Department from farmers in regard to the rapid corrosion of steel of modern manufacture used for various purposes, and especially for wire fencing. As the same difficulty has been constantly met in the use of corrugated iron and steel culverts for road drainage, it was decided to begin an investigation of the entire subject. The intention has been not only to get at the facts in the case, but also to aid as much as possible in bringing about an improvement in the rust-resisting quality of iron and steel used for the special purposes mentioned above.

Coincidentally with the beginning of the investigation inaugurated by the Office of Public Roads much attention began to be given to the same subject by a number of prominent metallurgists and chemists, both in this country and abroad. The American Society of Mining Engineers, at their Washington meeting, held in May, 1905, engaged in a discussion of the relative corrosion of iron and steel, and a vigorous debate followed the presentation of several papers on the same subject at the meeting of the American Society for Testing Materials, held at Atlantic City in June, 1906. The subject was considered so important that the latter society appointed a special committee of ten members to make an investigation of it.^a

In the Farmers' Bulletin mentioned above, on the corrosion of fence wire, special attention was given to the subject of electrolysis and its effects on wire. The suggestion was made that lack of homogeneity in the distribution of impurities in metal made by rapid modern processes might be at the bottom of the trouble. Some objection has

^a Prof. W. H. Walker, of the Massachusetts Institute of Technology, a member of this committee, has for some time past been making an independent investigation of the cause of the corrosion of iron. The writer has reason to believe that the results of Professor Walker's work will be found to confirm in a large measure the observations recorded in this bulletin. Although contemporaneous, the two investigations have been carried on quite independently, except in regard to the development of the ferroxyl indicator.

been raised to this suggestion on the ground that, although electrolysis probably plays a large part in the rusting of water pipes and structural iron in the neighborhood of electric conduits, it is unlikely that it can be considered a prime cause of the rusting or corrosion of iron and steel under all circumstances. Nevertheless, acting on the suggestion made in this Farmers' Bulletin, some of the manufacturers have made a determined effort to turn out a metal more resistant to corrosion, and the present indications are that these efforts have not been unsuccessful.

In 1894 and 1895 a series of papers was contributed to the Transactions of the American Society of Mechanical Engineers by M. P. Wood^a under the title "Rustless Coatings for Iron and Steel." In these papers all that was known up to that time on the cause and cure of corrosion is presented and ably discussed. On page 1070 of the Transactions for 1894 this author states:

That there is a continual electrical action of a most complex character present in all boilers under steam can scarcely be doubted, and the same action, but less apparent, is possibly present in all constructions of iron when the different members formed of iron and steel of various compositions, made by different processes after various torturing methods of manufacture to bring them to the desired shape, are assembled and put into duty under strains and conditions foreign to their nature. It would be strange indeed did not some electrical energy manifest itself and call for some palliative if not protective means of arresting decay.

It is well known that the various kinds of merchantable iron and steel differ within wide limits in their resistance, not only to the ordinary processes of oxidation known as rusting, but also to other corrosive influences. It is also true that different specimens of one and the same kind of iron or steel will show great variability in resistance to corrosion under the conditions of use and service. The causes of this variability are undoubtedly numerous and complex, and it is safe to say that the subject is not nearly so well understood at the present time as it should be.

In regard to two points all investigators are agreed, and as these furnish at least some common ground it is interesting to record them before proceeding to a discussion of the points at issue. Iron can not rust in air or oxygen unless water is present, and on the other hand, it can not rust in water unless oxygen is present. An interesting summary of the opinions held by various authorities prior to 1903 has been given by Mugdan,^b but although a number of investigators have worked on the problem since that time, the fundamental reactions which take place when a bright strip of iron immersed in water becomes coated with the red hydroxide known as rust are still a subject of controversy.

^a Am. Soc. Mech. Eng., Trans. 1894, 15, 998; *ibid.*, 1895, 16, 350, 663.

^b Zts. Elektrochemie, 1903, 9, 442.

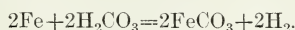
Three separate theories which, though they all more or less overlap, nevertheless involve distinctly different reactions, have been advanced and strenuously defended in the effort to furnish an explanation for the rusting of iron. These may be stated as the carbonic-acid, the hydrogen-peroxide, and the electrolytic theories.

Before any distinct progress can be made in the manufacture of metal that shall be more than ordinarily resistant to corrosion, it is of great importance that the underlying causes of oxidation should be clearly understood. It is the object of this paper to discuss the different theories and to present certain evidence recently obtained which bears directly upon the subject.

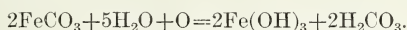
THE CARBONIC-ACID THEORY.

The carbonic-acid theory is the one most generally held, and usually presumes that without the interaction of carbonic or some other acid the oxidation, or better, the hydroxylation, of iron can not take place. The theory is best set forth in the words of a textbook recently published.^a

The process of rusting is a cyclical one, and three factors play an important part: (1) An acid, (2) water, (3) oxygen. The process of rusting is always started by an acid (even the weak carbonic acid suffices); the acid changes the metal to a ferrous salt with evolution of hydrogen:



Water and oxygen now act upon the ferrous salt, causing the iron in this salt to separate out as ferric hydroxide, setting free the same amount of acid which was used in forming the ferrous salt:



The acid which is set free again acts upon the metal, forming more ferrous salt, which is again decomposed, forming more rust. A very small amount of acid, therefore, suffices to rust a large amount of iron. If the acid is lacking, the iron will not rust. If we desire to prevent this rusting, we must neutralize the acid, e. g., add milk of lime. Iron remains bright under an alkali.

Probably no better example than this could be cited to show the textbook tendency to supply a complete explanation of a well-known phenomenon, the underlying causes of which are still imperfectly understood. Although the above explanation is sufficiently plausible, and in spite of the fact that carbonic acid, as well as other acids, do act a part in the ordinary rusting of iron, it will presently be shown that iron readily oxidizes, not only when carbonic acid is entirely absent, but also in dilute alkaline solutions. It is only when the hydroxyl ions supplied by an alkaline solution have reached a certain concentration that rusting is entirely prohibited.

^a Treadwell and Hall, Analytical Chemistry, 1907, p. 92.

The carbonic-acid theory was founded originally on the investigations of Crace Calvert,^a as interpreted by Crum Brown.^b It has also more recently been vigorously defended by Moody,^c who insists that with water and oxygen quite free from carbonic acid iron can not rust. This view is, however, not shared by Dunstan, Jowatt, and Goulding,^d or by Whitney^e or Cribb,^f all of whom give experimental evidence to show that rusting takes place rapidly in the absence of carbonic acid, provided liquid water and oxygen are present. The experiment of Dunstan and his co-workers was so carefully carried out that there seems to be no doubt that if carbonic acid plays any rôle whatever it is an unimportant one, and that rusting can go on with extreme rapidity in its absence.

In order to confirm this conclusion, the following experiment was made by the writer:

The Jena glass flasks *A*, *B*, and the beaker *C*, shown in figure 1, were nearly filled with freshly distilled water and boiled vigorously for one-half hour.

While the boiling was still proceeding bright polished strips of charcoal iron and steel were slipped into flasks *A* and *B* and the rubber stoppers, which had been previously cleaned by prolonged boiling in pure water, tightly inserted. After boiling for fifteen minutes longer the clamp at the end of tube *D* was opened

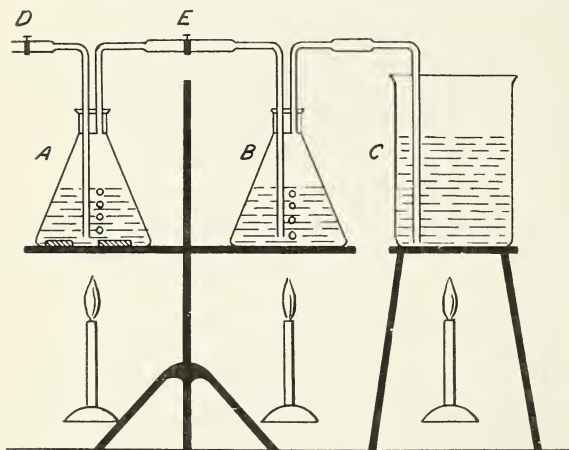


FIG. 1.—Apparatus to show the action on iron of pure water and oxygen.

for a moment and the back pressure allowed to drive any last traces of air from the tube. After tightly closing the clamp again, the lamps under flasks *A* and *B* were removed, while the water in *C* was still kept boiling. Boiled water immediately sucked back until the whole apparatus was completely filled, no trace of air being present. At all events, no slightest trace of rust appeared on the bright metal

^a Manchester Lit. Phil. Mem., 1871, 5, 104.

^b Jour. Iron and Steel Inst., 1888, 129–131.

^c Proc. Chem. Soc. (Lond.), 1906, 22, 101.

^d Jour. Chem. Soc., Lond., 1905, 87, pt. 2, 1548.

^e Jour. Am. Chem. Soc., 1903, 25, 394.

^f The Analyst, 1905, 30, 232.

strips when kept indefinitely under this boiled water. Pure oxygen from a cylinder was now washed perfectly free from last traces of carbonic acid by passing the gas through a train of wash bottles containing caustic potash, barium hydroxide, and limewater. On allowing this carefully purified oxygen to enter at *D* and bubble through the system of flasks, rust appeared on the bright metal surfaces in five minutes or less and in one hour had become deep and heavy. The action, just as in Dunstan's experiments, did not take place evenly all over the surface, but in patches, which had the appearance of a more or less regular pattern following the physical structure of the metal. This experiment has been frequently repeated, with every possible precaution to avoid the entrance of even the smallest trace of carbonic acid. On numerous occasions a few drops of phenolphthalein indicator was added to the boiling water in the three flasks, and invariably a pink color developed, proceeding from the metallic surfaces. This effect will be discussed at length further on and is mentioned at this place as contributory evidence that carbonic acid is not necessarily present, as Moody believes, before any reaction between iron, water, and oxygen can take place.

If pure, dry carbonic acid gas, freed from oxygen by passing through several wash bottles containing pyrogallie acid dissolved in sodium bicarbonate solution, was substituted for the pure oxygen gas and allowed to enter through tube *D*, no perceptible action took place on a bright piece of steel after several hours, although there can be no doubt that iron passed to a slight extent into solution as ferrous carbonate. Finally, if pure oxygen was allowed to enter at the same time and mingle with the carbonic acid, corrosion began in a short time. There was, however, a difference in the appearance of the rust that was formed with and without the interaction of carbonic acid. In the presence of carbonic acid the characteristic blue-green gradually changing to the red color peculiar to rust was observed. This appearance, as Moody truly observes, invariably accompanies the early stage of attack when iron is rusting in the presence of carbonic acid. In the experiments in which pure oxygen alone was permitted to enter the apparatus the blue-green initial stage of oxidation was never observed, the red ferric hydroxide making its appearance from the first, as it usually does, in normal cases of atmospheric rusting of bright iron surfaces.

It may be doubted whether it is possible to boil out all carbonic acid from the water contained in the apparatus shown in figure 1. Granting that this is the case in regard to last traces, it is easily shown that the hydrogen ions which would be supplied by a minute quantity of carbonic acid are of no more importance than the hydrogen ions supplied by the normal dissociation of pure water and that the

assumption that carbonic acid must be present is quite unnecessary. Whitney^a shows this very clearly in the following paragraph:

Assuming the laws of Henry and Dalton to apply to the solubility of carbonic acid gas in water, also that the solubility of the pure gas under ordinary pressure is one volume for one volume of water (which is correct at 15° C.), and, finally, that the normal content of carbonic acid in the atmosphere is 2 parts in 10,000 by volume, we should expect water in equilibrium with air containing this concentration of carbonic acid to contain 0.0002 volume carbon dioxide per volume of water. This corresponds to a concentration of the carbonic acid equal to 0.00001 mol per liter, or 0.00002 normal. From the dissociation constant 3040×10^{-10} determined by Walker,^b it follows that the first hydrogen of the acid is 16 per cent dissociated at this concentration. From this it follows that 10,000,000 liters of water containing carbonic acid in equilibrium with ordinary air at 15° contains 16 grams of hydrogen ions, or only 16 times as many as perfectly pure water contains. At the boiling temperature the carbon dioxide dissolved would probably yield a concentration of hydrogen ions even less than in pure water, for not only is the solubility of the gas greatly diminished, but the dissociation of water is greatly increased by rise of temperature. Moreover, the distilling water would rapidly reduce the concentration of any carbonic acid capable of dissolving in water at 100° C.

Moody prepared an apparatus in which the presence or subsequent entrance of even the smallest traces of carbonic acid was elaborately guarded against. The apparatus was constructed entirely of glass and was arranged in such a manner that polished cylinders of almost pure soft Swedish iron could be subjected to the action of water and air absolutely free from carbonic acid. Even with the very pure iron and with water which was undoubtedly rendered slightly alkaline by its intimate contact with a large surface of ordinary glass, Moody observed a slight amount of corrosion taking place on his bright iron surfaces. Still convinced, however, that the presence of carbonic acid was necessary before the slightest rusting effect could be produced, and believing that in some unknown manner an infinitesimal amount of this substance had eluded his vigilance, Moody began again with a new and quite extraordinary precaution. Before the bent tube which contained the polished specimen of iron was fused into its place in the apparatus it was partly filled with a 1 per cent solution of chromic acid, which just covered the iron. When the apparatus had been swept with air free from carbonic acid for three weeks, water was distilled through the tube containing the specimen until the chromic acid was all washed away. After this, as well as the added precaution of covering the ends of the iron cylinders with wax to prevent contact with the glass (as an interaction between glass and iron appeared also to cause corrosion even if no carbonic acid was present), the experiment was finally a complete success. In one case a current of air was passed through the apparatus for five weeks without even one speck of rust appearing.

^a Jour. Am. Chem. Soc., 1903, **25**, 397.

^b Zts. Phys. Chem., 1900, **32**, 137.

If Moody's experiment could be accepted as final, we must conclude that in an atmosphere that did not, like that of this earth, contain about 0.04 per cent of carbonic acid, the rusting of iron would be an unknown phenomenon.

It happens, however, that a recent observation of the writer explains the negative result obtained by Moody, without any reference whatsoever to the carbonic acid theory of rusting. It has long been known that rusting is inhibited and that polished iron will remain bright indefinitely in alkaline solutions, provided they are sufficiently concentrated. This is also true of all solutions of salts of strong bases and weak acids which hydrolyze to an alkaline reaction.^a This fact has been eagerly seized upon by the adherents of the three theories, as it can be made to fit in more or less well with them all. Thus, alkalis absorb carbonic dioxide, and therefore carbonic acid is prevented from carrying on its work of destruction. The added fact that fully saturated bicarbonate of soda also provides full protection to iron, even in fairly dilute solution, which would seem to be a stumbling block, has not shaken the faith of the devout believers in the carbonic acid theory.

The adherents of the peroxide theory claim that iron can not rust unless hydrogen peroxide is formed as a transition step in the reaction. As hydrogen peroxide is more or less unstable in alkaline solutions it is claimed that iron should not rust when immersed in them. The added fact that the rusting of iron is actually accelerated by solutions of potassium iodide, iodine, dilute potassium permanganate, and other substances which also destroy hydrogen peroxide, must apparently be accepted as an exception which proves the rule. The theory of electrolysis alone finds no difficulty in appropriating the facts of the alkali inhibition of oxidation. The full discussion of this point, however, must be postponed to a later portion of this bulletin.

As far as the writer is aware Dunstan and his co-workers were the first to make use in a theoretical discussion of the fact that solutions of chromic acid, potassium chromate, and potassium bichromate exercise a complete protection from rust to the surfaces of iron specimens immersed in them. It is probable, however, that the protective power of the chromates and some other oxidizing agents has been known and to some extent made use of in a practical way for a long time^b past. Wood stated in 1894 that a few substances, such as red lead, pyrolusite, the bichromate of potash, and chromate of lead, were gradually coming into use for anticorrosive paint compounds, and that their future use for this purpose was assured. This peculiarity of the chromates was interpreted by Dunstan as furnishing a

^a Zts. Elektrochemie, 1903, 9, 446.

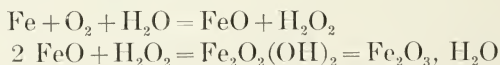
^b Am. Soc. Chem. Eng., Trans. 1894, 16, 384.

proof of the peroxide theory, as it is well known that hydrogen peroxide is destroyed by chromic acid and its salts.

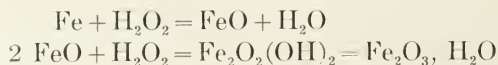
The writer has gone a step further and observed that the protection afforded by chromic acid and its salts differs from that of the alkalis in that the passivity is in a sense acquired by the surface of the iron and lasts for long periods, although the chromated specimens may have been washed with all possible care and even wiped with a cloth. In the writer's experiments all chromating has usually been done by immersing polished specimens of iron and steel in a strong solution of potassium bichromate for a number of hours, generally overnight. Steel wire nails treated in this way have been kept under water in vessels open to the contact of air and carbonic acid for many weeks without developing the slightest speck of rust or tarnish on their polished surfaces. In addition to this, polished specimens which have been chromated have been kept in moist air for weeks at a time without losing their passive condition. This astonishing phenomenon is so easily and quickly demonstrated by any one who cares to make a trial of it that it is not necessary in this place to include evidence to support the statement made above. The subject will be taken up in detail later on, and it is only mentioned here to show that Moody's experiment does not prove that the presence of carbonic acid is necessary before iron can rust. It must of course be admitted that the presence of hydrogen ions will hasten the corrosion of iron, and therefore the presence of a small amount of carbonic acid plays a minor rôle. The point that is made is that carbonic acid is not necessary, and that rusting can go on with extreme rapidity without it. If Moody had used pure oxygen instead of air he would undoubtedly have rusted his specimens in spite of their having been first chromated.

THE PEROXIDE THEORY.

Dunstan, Jowett, and Goulding based their peroxide theory of the rusting of iron on the general well-known theory of oxidation advanced by Traube.^a Thus the chemical reactions concerned in the formation of iron rust should be written:



The excess of hydrogen peroxide immediately reacts with the iron, forming a further quantity of rust:



Some of the evidence brought forward to substantiate this theory has already been referred to in a previous paragraph. It appears to

^a Ber. d. chem. Ges., 18, 1881.

derive some confirmation from the fact that delicate tests for hydrogen peroxide have been obtained during the slow oxidation of zinc and some other metals. On the other hand, in the case of iron these same delicate tests obstinately refuse to reveal even its transitory presence during the ordinary process of rusting. The theory has been criticised by Divers,^a Moody,^b and Cribb^c—the first named having pointed out that it is not tenable to argue that, because such substances as chromic acid and alkalis gradually destroy hydrogen peroxide, they must prevent its formation. For instance, ferrous sulphate is oxidized by free chlorine, but it does not prevent manganese dioxide and hydrochloric acid from reacting when brought together in its presence. Moreover, if the formation of hydrogen peroxide was a necessary stage in the rusting of iron and this is inhibited by certain substances which destroy hydrogen peroxide, why is not the inhibition extended to strong reducing agents generally? The theory is an interesting and suggestive one, but in the author's opinion is not supported by the facts.

THE ELECTROLYTIC THEORY.

From the standpoint of the modern theory of solutions, all reactions which take place in the wet way are attended with certain readjustments of the electrical states of the reacting ions. The electrolytic theory of rusting assumes that before iron can oxidize in the wet way it must first pass into solution as a ferrous ion. The subject has been interestingly treated by Whitney,^d who discussed it from the standpoint of Nernst's conception of the source of electromotive force between a metal and a solution. When a strip of metallic iron is placed in a solution of copper sulphate, iron passes into solution and copper is deposited, this change being of course accompanied by a transfer of electrical charge from the ions of copper to those of iron. Hydrogen acts as a metal and is electrolytically classed with copper in relation to iron. If, therefore, we immerse a strip of iron in a solution containing hydrogen ions, an exactly similar reaction will take place, iron will go into solution, and hydrogen will pass from the electrically charged or ionic to the atomic or gaseous condition. In such a system the solution of the iron and, therefore, its subsequent oxidation, must be accompanied by a "precipitation" or setting free of hydrogen. It is very well known that solutions of ferrous salts as well as freshly precipitated ferrous hydroxide are rapidly oxidized by the free oxygen of the air to the ferric condition, so that if the electrolytic theory can account for the original solution of the iron the explanation of rusting becomes an exceedingly simple one.

^a Proc. Chem. Soc. (Lond.), 1905, **21**, 251.

^b Jour. Chem. Soc. (Lond.), 1906, **89**, **90**, 720.

^c Analyst, 1905, **30**, 225.

^d Loc. cit. p. 10.

As iron has been shown by Whitney, Dunstan, and the writer to rust in the presence of pure water and oxygen alone, the electrolytic theory as a fundamental cause of the wet oxidation of iron must stand or fall on the determination of one crucial question, viz: Does iron pass into solution, even to the slightest extent, in pure water? If iron does dissolve, the electrolytic theory is so far satisfactory; if it does not dissolve, we must conclude that the oxygen finds some way of directly attacking the metal.

Almost everyone will admit that in the case of impure iron, with its unhomogeneous physical and chemical constitution, electrolysis will supervene, but it must be remembered that we are now concerned with the underlying cause of the wet oxidation or hydroxylation of iron, regardless of its state of chemical purity.

According to the dissociation theory, even the purest water contains free hydrogen ions to the extent of about 1 gram in 10,000,000 liters. If iron dissolves in the purest water it should be by interchange with hydrogen, and as Whitney^a has pointed out, pure water is to this extent an acid. In order to get experimental evidence on this crucial point, Whitney describes the following experiment:

A clean bottle was steamed out for a time to remove soluble alkali from the glass and was then filled with pure distilled water, which was kept boiling by passing steam through it for fifteen minutes. While still boiling, a bright piece of iron was placed in the bottle. A stopper (in some cases rubber and in others cork) carrying a tube open in a capillary several inches above the stopper was inserted into the bottle and firmly fastened in place, the water being kept boiling. Finally, the glass capillary was heated hot by means of a blowpipe and sealed by squeezing the walls together. The bottle was then allowed to cool to a temperature of about 80° C., and the neck of the bottle was finally covered with paraffin to prevent leaking. It was thought that in this way the oxygen, carbonic acid, and other gases in the water were completely removed. Bottles containing iron and sealed in this manner have stood without any visible change for weeks. In some cases a little air was subsequently admitted to bottles which had stood in this way with the iron apparently unaffected, and within a few minutes the water became cloudy and assumed a yellow color. Ordinary rust rapidly deposited upon the glass and in spots upon the metal. In fifteen or twenty minutes the production of rust throughout the bottle was perfectly evident. It seemed plain from the rapidity of formation of oxide and its precipitation on the glass that the iron had dissolved in the water before the addition of the air, and that the latter simply permitted the formation of the insoluble oxide.

Dunstan and his co-workers reviewed and repeated Whitney's experiment and failed to confirm his result. These investigators do not believe that hydrogen is evolved during the rusting of iron, or that iron dissolves even to the slightest extent in pure water. They also claim that the electrolytic theory affords no explanation that substances such as chromic acid and potassium bichromate inhibit the rusting of iron. The description of the experiment on which Dunstan

^a Loc. cit., p. 10.

based his opposition to the electrolytic theory is quoted verbatim, as follows:

A flask of 600 c. c. capacity, filled with distilled water, was boiled for fifteen minutes; two pieces of purified iron, each about $1\frac{1}{2}$ inches square, were then placed in the flask, and an india-rubber stopper carrying a glass tube which projected 7 to 8 inches above the stopper and ended in a capillary was fitted into the neck of the flask, the water being kept boiling continuously. The water was allowed to boil for five minutes longer, when the capillary was sealed and the stopper coated with paraffin wax. This flask was left at the ordinary temperature for three weeks, in the course of which no visible change occurred. It was then opened, when one-half of the liquid was quickly poured into a beaker, the other half being left in contact with the iron in the flask. The liquid in the beaker on exposure to the air showed no cloudiness, no yellow coloration, and no separation of rust. In fact, on testing the liquid for iron by the extremely delicate thiocyanate reaction not a trace could be detected. The pieces of iron in the open flask after an hour showed signs of rusting, just as in ordinary cases, but the phenomena described by Whitney were not observed. We are therefore unable to confirm Whitney's statement that liquid water alone is capable of dissolving even an infinitesimal quantity of iron. This being the case, the theory based on this statement becomes untenable.

It is quite clear that the point at issue is an important one, on which hangs the decision as between the two theories. In order to obtain

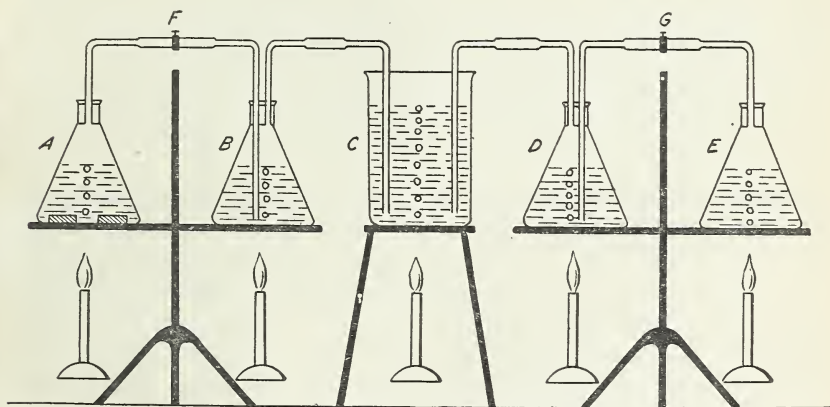


FIG. 2.—Apparatus used to determine the extent of the solubility of iron in pure water.

more light on the subject the writer devised the following experiment, which is sufficiently simple to be repeated by anyone without encountering any difficulties whatever. The apparatus used is shown in figure 2.

The two clean Jena glass flasks *A* and *B* are three-quarters filled with pure freshly distilled water. Two drops of an alcoholic solution of phenolphthalein indicator (1 gram in 100 c. c. pure alcohol) are added to the water in each of the flasks. The beaker *C* is more capacious than the flasks *A* and *B*. The flasks *D* and *E* are used in each experiment as blanks to check the results obtained. After connecting up as shown, the water in each vessel is simultaneously boiled

very vigorously until about one-quarter is boiled off. The rubber stopper in *A* is then lifted, and clean, polished strips of iron quickly slipped in. The stopper is again tightly inserted and the boiling continued for about fifteen minutes. The lamps under *A* and *E* are then extinguished, while the water in *B*, *C*, and *D* continues to boil. As soon as flasks *A* and *E* have sucked back boiling water so that they are completely filled, the lamps under flasks *B* and *D* are also extinguished. When *B* is quite full, flasks *A* and *B* are quickly cooled by surrounding them with cold water. The valve at *F* is then closed. By this means the bright specimens are immersed in water practically free from air, oxygen, or carbonic acid, and may be kept under observation for any desired length of time. This experiment has been repeated a great number of times with different samples of iron and steel, and no rusting has ever been observed unless air was allowed to enter.

It has been shown that the electrolytic theory of the wet oxidation of iron is based on the premise that iron must first go into solution, an equivalent amount of hydrogen being set free. The resulting ferrous hydroxide in solution betrays its presence by producing a pink coloration with the phenolphthalein indicator. In every experiment made the pink color was seen, although in some cases the color developed slowly and only after the lapse of a number of hours. That the color was not due to the action of the water on the Jena glass was shown by the fact that no color appeared on the blank side of the experiments.

Another simple experiment was made in order to determine the concentration of hydroxyl ions that must occur before a pink color can be distinctly seen. Five hundred and fifty c. c. of distilled water containing 1 c. c. of phenolphthalein indicator was boiled down in a Jena flask to 500 c. c. One one-hundredth normal potassium hydroxide solution was then run into the quickly cooled water from a burette. It was thus found that about 1 c. c. of one one-hundredth normal potassium hydroxide was the limit of the quantity necessary to produce a distinctly visible pink color; 1 c. c. of one one-hundredth normal potassium hydroxide contains 0.00017 gram of hydroxyl. This quantity in 500 c. c. of water represents a concentration of about 0.35 part of hydroxyl per million. Since the flasks shown in figure 2 contain when quite full 360 c. c., there must have been present a weight of hydroxyl ions approximately equal to $0.35 \times 360 \times 10^{-6} = 0.00012$ gram OH. This corresponds to an amount of ferrous iron dissolved equal to $11.2 \times 360 \times 10^{-6} = 0.00040$ gram Fe.

In referring to Dunstan's experiment it will be seen that he boiled two small pieces of iron $1\frac{1}{2}$ inches square for only five minutes in 600 c. c. of water. At the end of the test 300 c. c. was poured off to be

tested for iron. It is hardly likely under these conditions that, had this experimenter added phenolphthalein to the water, he would have reached the limit of visibility of the pink color. Granting, however, that he had reached this point, it is apparent that he was making tests for iron in a solution that contained in each centimeter no more than 0.000001 gram of iron. By carefully evaporating the entire 360 c. c. to dryness in a clean platinum dish, with especial precaution to avoid the entrance of dust, the writer has not only been able to show the presence of iron with the ordinary test reagents of ammonium thiocyanate and ferrocyanide, but has also quantitative evidence of the approximate correctness of the amount present, as estimated from the visibility of the color produced by phenolphthalein.

Six polished strips of iron, $2\frac{1}{2}$ by $\frac{1}{2}$ by $\frac{1}{16}$ inch, were boiled in flask *A* in the apparatus shown in figure 2, as already described. After the water in flask *B* had sucked back, flask *A* was allowed to stand until a pink color was just visible. The contents of the flask were then evaporated to dryness, the phenolphthalein burned off, and the residual ferric oxide weighed. The residue weighed 0.0006 gram, equivalent to 0.0004 gram of iron.

Since it was thought that some doubt might be felt whether even the small amount of phenolphthalein present could attack the iron, the experiment was repeated with iron and boiled water alone, but the results invariably showed that a small amount of iron had dissolved. In view of the ease with which these experiments can be confirmed it would seem needless to yield more space to this phase of the discussion. It appears to the writer to be demonstrated that Whitney was right in his assertion that iron goes into solution up to a certain maximum concentration in pure water, without the aid of oxygen, carbonic acid, or other reacting substances.

This point established, it becomes apparent that the rusting of iron is primarily due, *not to attack by oxygen, but by hydrogen ions*. Absolute confirmation of this view will be given later on.

STIMULATING AND INHIBITING EFFECTS OF CERTAIN SUBSTANCES UPON THE CORROSION OF IRON.

All substances in solution which contain hydrogen ions, such as acids, stimulate the corrosion of iron. This is also true of salts of strong acids and weak bases, which, though perfectly stable in a dry condition, hydrolyze in solution to an acid reaction; or which, though neutral in fresh solutions, undergo slow decomposition under the action of light, with the formation of acid salts or free acid. With certain exceptions, salts which are perfectly neutral in solution do not prevent oxidation but appear to aid it by increasing the electrolytic action. All substances which develop hydroxyl ions in solution, such as the alkalis or salts of strong bases with weak acids, to a certain

extent inhibit, and, if the concentration is high enough, absolutely prohibit the rusting of iron.

Under the electrolytic theory the explanation of the protection afforded by hydroxyl ions is a simple one. Owing to the small dissociation of water, hydrogen ions can not exist in a solution in which the hydroxyl ions are in excess. As hydrogen ions can not exist or be locally formed in sufficiently strong alkaline solutions, no attack is made upon the iron, which remains permanently unaltered. If, however, the concentration of the hydroxyl ions is not sufficiently great, electrolysis can go on with an apparent stimulation of the pitting effects similar to that produced by perfectly neutral electrolytes, such as sodium chloride.

As has already been noted, solutions of chromic acid and potassium bichromate inhibit the rusting of iron. In order to determine the concentration necessary to produce complete protection, a number of polished strips of two different samples of steel were immersed in bichromate solutions of increasing concentration, contained in tubes which were left quite open to the air. There were twelve tubes in each series, ranging by regular dilutions from tenth-normal down to ten-thousandth normal. At the end of two months the last four tubes showed graded rusting with accumulation of ferric hydroxide. No rusting had occurred in any of the solutions above tube No. 8, which contained six-hundred-and-fortieth normal bichromate, a strength corresponding to about 8 parts of the salt in 100,000 parts of water, or about 2 pounds to 3,000 gallons. Since solutions of bichromate do not hydrolize with an alkaline reaction, but on the contrary are usually slightly acid, some other explanation must be found for this remarkable phenomenon. On first thought it would seem a paradox that a strong oxidizing agent should have the effect of preventing the oxidation of iron, and yet this is precisely the case. If, however, the initial cause of rusting is the hydrogen ion, it is possible to believe that under certain conditions oxygen would prove the most effective of all inhibitors. As has been stated, Dunstan, Jowett, and Goulding have claimed that this peculiar action of chromic acid and its salts is due to the fact that they destroy hydrogen peroxide. This explanation is not satisfactory, as has been pointed out, and it is fair to inquire whether the electrolytic theory is capable of furnishing a solution of the problem. Furthermore, it will be shown that additional evidence can be brought forward which can not be made to apply to any other theory.

The writer has observed that if a rod or strip of bright iron or steel is immersed for a few hours in a strong (5 to 10 per cent) solution of potassium bichromate, and is then removed and thoroughly washed, that a certain change has been produced on the surface of the metal. The surface may be thoroughly washed and wiped with a clean cloth

without disturbing this new surface condition. No visible change has been effected, for the polished surfaces examined under the microscope appear to be untouched. If, however, the polished strips are immersed in water it will be found that rusting is inhibited. An ordinary untreated polished specimen of steel will show rusting in a few minutes when immersed in the ordinary distilled water of the laboratory. Chromated specimens will stand immersion for varying lengths of time before rust appears. In some cases it is a matter of hours, in others of days or even weeks before the inhibiting effect is overcome.

The passivity which iron has acquired can be much more strikingly shown, however, than by the rusting effect produced by air and water. If a piece of polished steel is dipped into a 1 per cent solution of copper sulphate, a 10-second immersion is sufficient to plate it with a distinctly visible coating of copper which can not be wiped off. A similar polished strip of steel which has been soaked over night in a concentrated solution of bichromate and subsequently well washed and wiped will stand from six to ten 10-second immersions in 1 per cent copper sulphate before a permanent coating of copper is deposited. Even a momentary plunging of the metal into the bichromate will induce a certain passivity, but the maximum effect appears to require a more prolonged contact with the solution.

The first explanation of this phenomenon which naturally presents itself is that a thin film of either oxide or chromate has been formed on the surface of the metal. It is almost inconceivable, however, if such a film is formed, that it can not be seen with the aid of a microscope. There is evidence which appears to indicate that no such film of oxide is formed. It is easy to cover polished iron with a visible film of oxide by simply flaming it gently in a Bunsen burner. Such films do not succeed in protecting the iron either from the rusting or the copper sulphate test. Still more convincing than this is the fact that if a polished surface which has been rendered passive by immersion in bichromate is heated to 100°C . for some hours, its passivity disappears and it again behaves in a normal manner. None of the oxides or chromates of iron are in any sense volatile compounds, so that if a solid but invisible film is really formed, it is in some manner dissipated by heat. Further than this, a chromated strip of iron which is kept in a vacuum soon loses its passivity, whereas a similar strip kept under ordinary conditions remains passive for long periods.

The passivity of iron was discovered by Keir in 1790.^a Since the phenomenon is produced only by strong oxidizing agents or by galvanic contact when oxygen can separate on the iron, it was explained by Faraday, Wiederman, and others^b as due to a thin oxide film.

^a Phil. Trans. (Lond.), 1790, 359.

^b Dammer's Anorg. Chem., 1893, v. 3, p. 294.

From the evidence given above, however, it seems that the passivity of iron is better explained as a polarization effect produced by the separation and retention of oxygen on the surface of the metal. If the rusting of iron is due primarily to the action of hydrogen ions, iron in the condition of an oxygen electrode should be more or less well protected from electrolytic attack.

Keir^a observed that polished iron which had been immersed in red fuming nitric acid was altered in some manner so that its power of precipitating silver and copper from their solutions was inhibited, and this occurred, in the discoverer's own words, "without the least diminution of metallic splendour or change of color." In the writer's experience red fuming nitric acid does not produce the passive condition as successfully as solutions of chromic acid and its salts. Mugdan discussed the passivity acquired by iron which was immersed in fuming nitric or sulphuric acids and concluded that it was not due to the formation of an oxide film, but was a true passivity in the sense of an ennobling (Veredlung) of the metal,^b accompanied by a low electrical potential.

Moody^c asserts that potassium bichromate prevents the formation of rust, owing to the fact that it slowly dissolves iron and its hydroxides. He observed that the addition of ammonia to solutions of chromic acid and its salts which had been allowed to act on iron produced precipitates of hydroxide. This point has been carefully investigated by the writer, with the following results: Iron which is free from manganese is not attacked by solutions of bichromate, even if boiled for days in a flask fitted with a return condenser. Manganese is, however, readily soluble in bichromate solutions, and therefore iron rich in manganese yields a sufficient amount to the solvent action to produce a small amount of brownish manganese hydroxide when the bichromate solution is poured off, made slightly ammoniacal, and allowed to stand. If metallic manganese is boiled in bichromate solutions it dissolves readily, and subsequent addition of ammonia produces an abundant precipitate of brown manganese hydroxide.

If polished iron is allowed to stand for some time in standard tenth-normal potassium bichromate solution, the oxidizing strength of the latter as measured by its titration value is slightly reduced without the solution of the iron or the production of any visible effect. Under the same conditions a standard solution of neutral potassium chromate is slightly reduced with the appearance of a small amount of chromic hydroxide. In fact, all the evidence obtainable points to the abstraction by the iron of some of the

^a Dammer's Anorg. Chem., 1893, v. 3, p. 294. ^b Zts. Elektrochemie, 1903, 9, 454.

^c Loc. cit., p. 15.

available oxygen of chromic acid and its salts without the formation or solution of iron oxide films.

In order to show beyond doubt that an oxygen electrode is formed by immersing iron in a strong solution of bichromate the following experiment was made: Two polished steel electrodes were prepared and chromated by immersion for a number of hours in a strong solution of potassium bichromate. The prepared electrodes were then thrust tightly through a rubber stopper which closed the Jena flask *A*, which was then filled with pure freshly boiled distilled water in the manner shown in figure 1. The electrodes were then attached to the poles of a primary battery at about 2 volts potential. At the end of half an hour, although the potential was not sufficient to disengage bubbles of gas and no visible change had occurred, the electrode which was connected to the zinc pole of the battery had lost its passivity, the other retaining it.

It might still be objected that if a film of oxide had been formed it might suffer reduction at the negative pole. It is, however, very easily shown that electrodes which have been oxidized by gentle heating are not reduced under the conditions of this experiment.

Wood ^a in 1895 commented on the power of paints and pigments containing certain oxidizing agents, notably potassium bichromate and lead chromate, to form on iron and steel surfaces a thin coating of oxide which so effectually protects the metallic surfaces from corrosion that after the removal of the paint the metal still resists atmospheric effects for a long time, as well as the stronger effect of immersion in sea water or acidulated waters and sulphurous and other vapors. This action, Wood adds, is very obscure and not thoroughly understood; but the fact remains, and extended experiments in this field only demonstrate its presence and usefulness.

The oxide film theory has been held for many years to account for the passivity of iron, but in the writer's opinion the protection afforded by certain oxidizing agents is electro-chemical and not mechanical.

THE ACTION OF HYDROGEN PEROXIDE ON IRON.

Perhaps the most conclusive proof that electrolytic action must take place before rusting can occur is given by an experiment of Moody's, which has been repeated and confirmed by the writer. Dunstan and his co-workers claimed that when iron is placed in hydrogen peroxide the metal is rapidly oxidized, with formation of ferric hydroxide. As Moody has pointed out, commercial hydrogen peroxide is invariably acid and contains impurities. In perfectly pure hydrogen peroxide bright iron will catalytically disengage

^a Amer. Soc. Mech. Eng. Trans., 1895, 16, 671.

oxygen and retain its polished surface unacted upon. It is not an easy matter to prepare a perfectly neutral pure solution of hydrogen peroxide, but it can be accomplished by two fractional distillations at 85° C. under reduced pressure (700 mm.) of commercial dioxygen. Before distilling the second time the solution should be made barely alkaline with a few drops of one-hundredth normal potassium hydroxide. In a pure neutral 1 per cent solution of hydrogen peroxide thus prepared, Moody's observation was confirmed. Iron immersed in the solution remained bright for a protracted period. Hydrogen ions do not exist in a pure neutral solution of peroxide; therefore neither solution of iron nor electrolysis can take place. If the flask containing the specimens covered by pure hydrogen peroxide solution is connected to a vacuum pump, oxygen is disengaged freely and boils off the surface of the metal without the appearance of the slightest speck of rust.

Reduced to its simplest terms, the following explanation of the rusting and corrosion of iron seems to the writer the only one that is tenable. In order that rust should be formed iron must go into solution and hydrogen must be given off in the presence of oxygen or certain oxidizing agents. This presumes electrolytic action, as every iron ion that appears at a certain spot demands the disappearance of a hydrogen ion at another, with a consequent formation of gaseous hydrogen. The gaseous hydrogen is rarely visible in the process of rusting, owing to the rather high solubility and great diffusive power of this element. Substances which increase the concentration of hydrogen ions, such as acids and acid salts, stimulate corrosion, while substances which increase the concentration of hydroxyl ions inhibit it. Chromic acid and its salts inhibit corrosion by producing a polarizing or dampening effect which prevents the solution of iron and the separation of hydrogen.

DEMONSTRATION OF ELECTROLYTIC ACTION.

Early in this investigation the writer observed that whenever a specimen of iron or steel is immersed in water or a dilute neutral solution of an electrolyte to which a few drops of phenolphthalein indicator had been added, a pink color is developed. If the solution is allowed to stand perfectly quiet it will be noticed that the pink color is confined to certain spots or nodes on the surface. The pink color of the indicator is a proof of the presence of hydroxyl ions and thus indicates the negative poles. Many persons who are interested in the metallurgical problems connected with the iron and steel industry may not be familiar with the modern theory of indicators, and therefore an explanation of the manner in which phenolphthalein shows the presence of hydroxyl ions by the formation of a pink color will not be out of place. Phthalic acid was first prepared by

Laurent in 1836 by the oxidation of naphthalene, and was first called naphthalinic acid. It was afterwards shown that the compound was not directly related to the naphthalene structure and Laurent changed the name to phthalic acid, the derivatives of which became known later as phthaleins. Phenolphthalein is a product which is formed by the condensation of two molecules of phenol or carbolic acid with the anhydride of phthalic acid. It is in its nature so weak an acid that it is not dissociated in solution, and as the molecule is colorless, no color is seen when it is added to a perfectly neutral solution. If, however, an alkali is added the corresponding salt of the weak acid is formed, which immediately dissociates with the formation of a colorless metallic cation and the strongly rose-colored organic anion. Thus all hydroxides of basic elements will show the pink color in solution, even when present in only the slightest excess. On this account phenolphthalein is an exceedingly delicate indicator of the presence of hydroxyl ions.

Since phenolphthalein^a shows only the nodes where solution of iron and subsequent oxidation can not take place, Prof. W. H. Walker suggested the addition of a trace of potassium ferricyanide to the reacting solution, in order to furnish an indicator for the ferrous ions whose appearance mark the positive poles. If iron goes into solution, ferrous ions must appear, which, with ferricyanide, form the well-known Turnbull's blue compound. Going a step further, Walker suggested stiffening the reagent with gelatin and agar-agar, so as to prevent diffusion and preserve the effects produced. For this combined reagent, which indicates at one and the same time the appearance of hydroxyl and ferrous ions at opposite poles, the writer has suggested for the sake of brevity the name "ferroxyl." The reagent is prepared and used in the following manner: A hot solution of the purest agar-agar or gelatin in distilled water is carefully neutralized with one-hundredth normal potassium hydroxide, using phenolphthalein as the indicator. When exact neutrality has been obtained a few drops of a dilute solution of potassium ferricyanide is added. When a layer of the reagent is poured into a dry Petri dish floating in ice water it should stiffen into a firm jelly in a few minutes. The polished specimens are laid carefully on the jelly and flooded with another layer of the reagent. After the preparation has hardened it should be covered and set away in a cool, dark place. In the course of a few hours the negative and positive zones will begin to develop in red and blue. If the reagent has been properly pre-

^a Phenolphthalein is used to a large extent in empirical tests, as in dairying, the cement industry, soil examinations, etc. The name is cumbrous if not alarming to the layman, while the chemist does not need to be reminded of the origin of the compound each time he has occasion to speak of it. A shortening of the name of the indicator to "phenolin" would be a decided improvement.

pared the color effects are strong and beautiful. In the course of a few days the maximum degree of beauty in the colors is obtained, after which gradual deterioration sets in. The best results obtained by the writer are shown in Plates I, II,* and III.

The areas which show with sharp outlines in the reproduction are the blue positive nodes, while the pink negative nodes appear with hazy outlines. In the pink zones, as would naturally be expected, the iron remains quite bright as long as the pink color persists. In the blue zones the iron passes into solution and continually oxidizes, with a resulting formation of rust. Even the purest iron develops the nodes in the ferroxyl indicator, but impure and badly segregated metal develops the colors with greater rapidity and with bolder outlines. This result would of course be expected, as in pure iron the formation of poles would be conditioned by a much more delicate equilibrium than in impure iron, where changes in concentration of the dissolved impurities would stimulate the electrolytic effects. Even so-called chemically pure iron contains small quantities of dissolved gases, and it is not improbable that even slight variations in the physical homogeneity of pure iron will occasion the electrolytic effects which are made visible by this delicate reagent.

It has been noted by a number of investigators that different samples of iron and steel do not rust in the same way when subjected to the action of water and air. While some samples show localized electrolytic action, as indicated by deep pitting, others become covered with a more or less homogeneous coating of hydroxide, which shows little or no tendency to localize in spots or nodes. The question naturally arises: In what respect do these two methods of rust formation differ? A close inspection of Plate III is suggestive if not conclusive of the answer in this respect. The photographic reproduction exhibits an effect which is frequently observed in the ferroxyl tests. When the colors first developed, two dark blue nodes formed at the opposite ends of the test piece, with a large pink area in the center, where for a time the metal remained quite bright. Very shortly, however, the poles changed, and the pink central area disappeared and gave way to a large blue node which enveloped three-quarters of the test piece, with a small opposed pinkish spot. Again and again a reversal and change of poles took place, and at least five such changes are clearly shown in the photograph. As a result of this action the metal strip was rapidly covered over its entire surface with the same superficial, loosely adherent coating of hydroxide, which is obtained in many cases when certain samples of iron and steel are allowed to rust under a layer of water. It is presumable that as the surface of the metal is eaten into by the solution of the iron at the positive poles, a new condition of equilibrium occurs, resulting in changes and even reversals of the positive and negative nodes. This would indicate



IRON AND STEEL NAILS IN FERROXYL REAGENT.

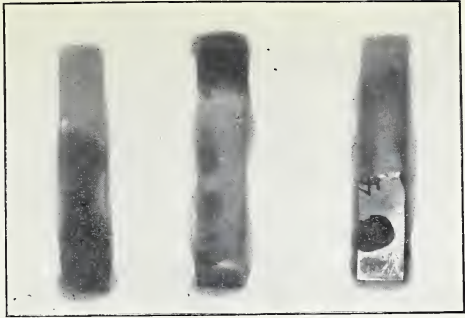


FIG. 1.—WROUGHT IRON, CHARCOAL IRON, AND STEEL IN FERROXYL.



FIG. 2.—STEEL NAILS IN FERROXYL REAGENT.

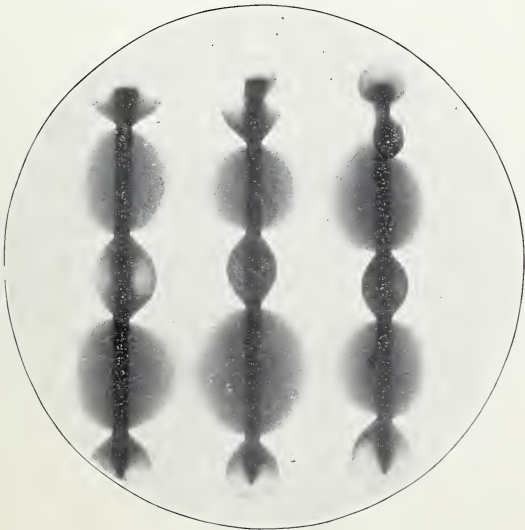


FIG. 3.—STEEL WIRE NAILS IN FERROXYL REAGENT.





STRIP OF STEEL IN FERROXYL REAGENT, SHOWING FREQUENT REVERSAL OF POLES.

that in the case of metals which suffer from local action or pitting the segregation conditions are of a different nature from those which exist in the case of metals which rust more evenly. A rough analogy may be drawn by imagining an imperfect mixture of black and white sand, the respective grains of which may lie in streaks, spots, and layers, or may tend to arrange themselves in some more or less uniform relation to each other. The best demonstration that the rusting and corrosion of iron and steel in all its forms is essentially an electrolytic phenomenon is afforded by the fact that it has not as yet been possible to find a specimen of such purity that no trace of positive and negative nodes will be formed in the ferroxy! indicator.

APPLICATION OF ELECTROLYTIC THEORY.

We may now apply the electrolytic theory to the actual results obtained in the ordinary rusting of iron. If a section of rolled metal, such as sheet or plate, is immersed in water, if the electrolytic theory is correct, rusting must take place with the establishment of positive and negative spots or areas. At the positive points iron will pass into solution and be rapidly oxidized to the loose colloidal form of ferric hydroxide which is characteristic of rust formed under these conditions. It is a well-known fact that colloidal ferric hydroxide will move or migrate to the negative pole if subjected to electrolysis. We may therefore consider the possibility of two separate effects that may be produced, viz, when a positive center is surrounded by a negative area, and vice versa. These two conditions may be graphically represented by the two circles *A* and *B* shown in figure 3.

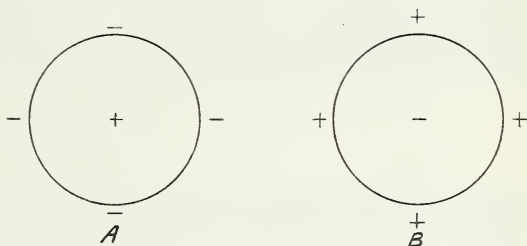


FIG. 3.—Diagram illustrating electrolytic action on the surfaces of iron and steel.

Now, as rusting proceeds we should expect in the case of *A* that the ferric hydroxide would be piled up in a crater formation, while the metal is eaten out at the center. In the case of *B* the effect would be reversed, and while the metal would be attacked in the surrounding area the hydroxide would be piled up in a cone at the center. That this is precisely what is taking place whenever a sheet of metal rusts under water a low-power microscope very clearly shows. In Plates IV and V the writer has succeeded in showing the existence of both the craters and cones as they formed on the surface of a piece of wrought-iron boiler plate. In Plate IV, figure 1, a typical crater surrounding the point of pitting is shown, while in figure 2 an excellent

example of the cone appears. Both are photomicrographs magnified about 45 diameters. The source of light was on the right in each case and the shadows indicate the crater and cone formation, which is so clearly discernible under the microscope. Plate V is from photographs of the rusted metal, showing the craters and cones as they appeared with very low magnification.

Plate VI shows the surfaces of strips of Bessemer steel (s), puddled wrought iron (z), and charcoal iron (c), prepared in the following manner: The respective samples were turned off in a lathe to a bright, smooth finish; they were then immersed under a thin layer of the ferroxyl reagent and allowed to stand quietly for several days. At the end of this time the surfaces were wiped clean. The electrolytic effects, which had been active on all three metals, are very well illustrated. The light portions show the negative areas, where little or no rusting took place, while the dark spots and areas show the special points of attack, with the pitting effects. The etching is not, of course, deep in the case of any of the three samples and should not be understood as showing the relative rate of corrosion of the different types of metal. The specimens simply serve as a demonstration that the rusting in each case has been accompanied by electrolysis.

In Plate VII, is shown a photograph of the actual pitting of a boiler tube, which failed, after eighteen months' service, in a water-tube type of marine boiler. The conclusion that pitting was due to electrolysis seems justified by comparing this photograph with those shown in Plate V.

The evidence advanced in the preceding pages appears to the writer to confirm the conclusion that the whole subject of the corrosion of iron is an electro-chemical one, which can be readily explained under the modern theory of solutions. It is an undeniable fact that some irons and steels suffer corrosion very much more rapidly than others, and the underlying causes for these differences constitute one of the important problems of modern metallurgy.

Although the discussions brought forward in this bulletin are mainly theoretical in their nature, it is quite apparent that they also have an indirect practical bearing. Before advance can be made in overcoming the difficulties in the way of manufacturing iron which shall have the maximum resistance to corrosion, as well as the preservation of the metal under the conditions of service, the underlying causes must be thoroughly understood. If we accept the electro-chemical explanation of the corrosion of iron, there can be no doubt that conditions which inhibit electrolytic effects also inhibit corrosion, and vice versa. The purer the iron in respect to certain other metals which differ electro-chemically from iron and the more carefully lack of homogeneity and bad segregation are guarded against

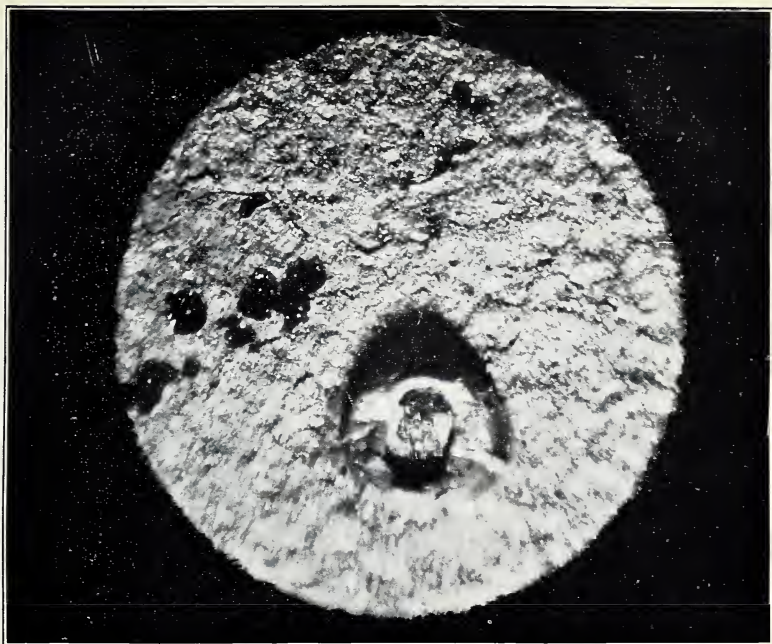


FIG. 1.—FORMATION OF CRATER WITH PITTING EFFECT IN CENTER.
(ENLARGED 45 DIAMETERS.)

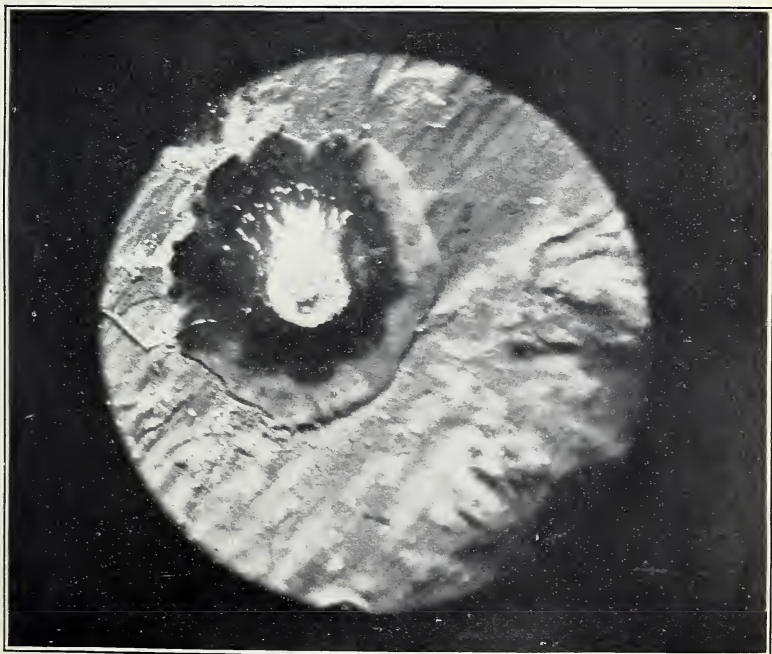
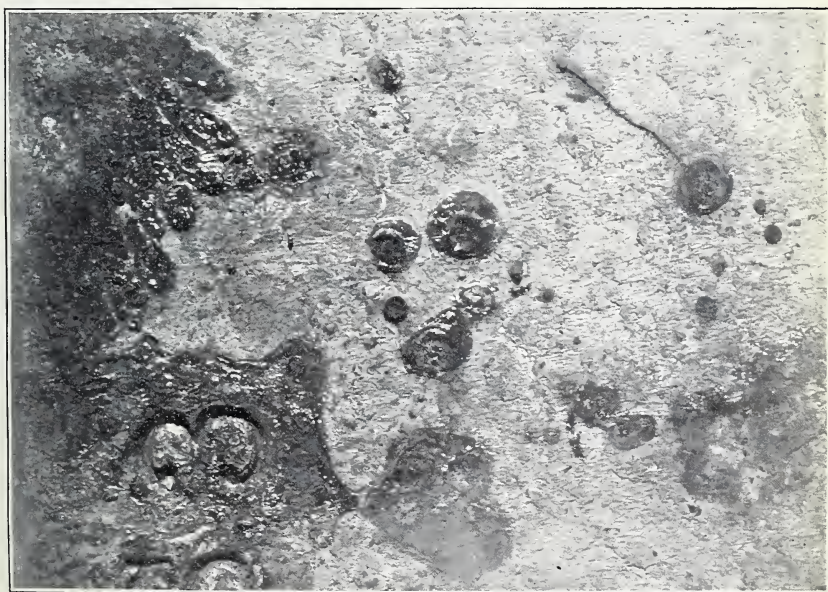
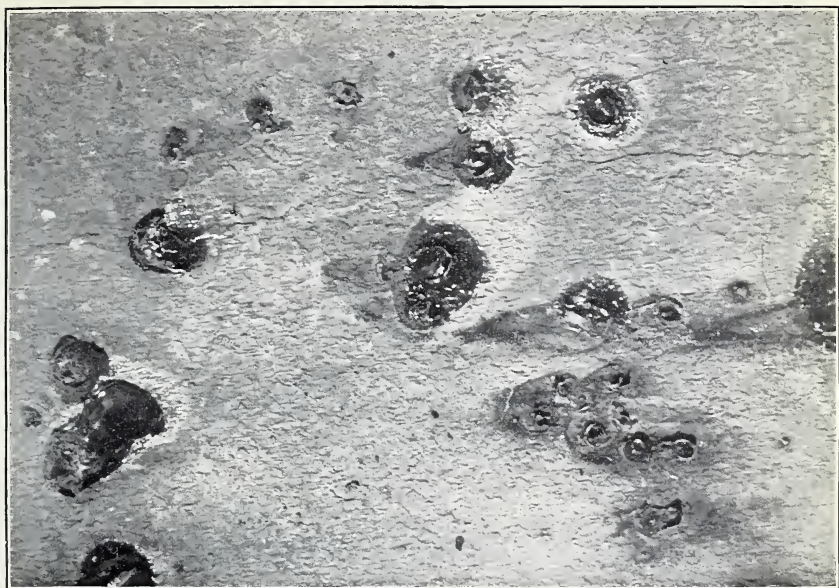


FIG. 2.—FORMATION OF CONE WITH PITTING EFFECT IN SURROUNDING
AREA. (ENLARGED 45 DIAMETERS.)



PHOTOGRAPHIC REPRESENTATION OF RUST SPOTS FORMED ON THE SURFACE OF IRON.



S



Z



C

ETCHING EFFECT PRODUCED ON POLISHED SURFACES OF IRON AND STEEL BY IMMERSION
IN FERROXYL REAGENT.



PITMARKS ON SECTION OF BOILER TUBE.



the less likely are the electrolytic effects to become serious. These points constitute the essential problems which confront the manufacturer who desires to make a product which shall have a high resistance to corrosion. The user and consumer, however, are interested in the protection of the various types of merchantable iron and steel which are available under market conditions at the present time. In short, protective coatings and palliative methods of treatment are in greater demand to-day than ever before. From the standpoint of the electrolytic theory many suggestions for experiment under the conditions of service present themselves. The fact that hydroxyl ions inhibit the rusting of iron has been made practical use of for a long time past, and it is not unusual to add caustic alkalis to boiler waters for this reason. This, however, frequently causes trouble from foaming and, as Cribb^a has shown, if an insufficient amount of alkali is present the pitting effect is accentuated rather than inhibited. This observation is in accord with the theory that the hydroxyl ions must reach a certain concentration, which varies with different conditions, before entire prohibition of the electrolytic effects is obtained.

At concentrations much below those necessary to prohibit electrolysis the action is similar to that obtained by adding a neutral electrolyte to the water, i. e., the electrolytic effects are localized if not stimulated. There should be many cases, however, where the property of alkalis to inhibit corrosion could be made of more practical use than has been done. Whenever iron posts or standards are set directly in the ground instead of being embedded in concrete, the liberal use of slaked lime should be beneficial.

The expedient of using metallic zinc in boilers to overcome the local electrolytic effects in the iron by producing a still greater electrolytic effect at the almost exclusive expense of the more positive zinc is well known and has been in use for a long time. Although the theory on which the use of zinc for this purpose is based is sound, great difficulty has been encountered in maintaining good metallic contacts between sufficiently large surfaces of the two metals under the conditions which maintain in a boiler. From what has been shown in regard to the inhibitive action of the chromates it is not improbable, since such dilute solutions prevent electrolysis and corrosion, that the addition of small quantities of bichromate to boiler waters would be highly efficacious in preventing the rapid pitting which has caused so much trouble. It has lately been reported that steel boiler tubes used on vessels fitted with turbine engines suffered corrosion to the point of failure in from two to four months' service.^b This was found to be due to the fact that the steam, containing per-

^aLoc. cit., p. 15.

^bEng. News, 1907, 57, 426.

haps volatile acids, impinging on the bronze turbine blade, carried copper into solution and through the condensers into the boiler. Since iron does not change places with copper in dilute solution containing bichromate, it is possible that here again this salt would be found of practical value. That this statement is correct can easily be shown. If a bright piece of iron is immersed in a solution of copper sulphate so dilute as to show only a faint bluish tinge, the iron will nevertheless turn dark from precipitated copper in a very few moments. If now potassium bichromate is added in only just sufficient amount to give a yellowish instead of a bluish tinge to the solution, iron will remain bright and copper will not be deposited.

The experiment has been made by the writer of keeping iron and steel in dilute boiling solutions of bichromate for protracted periods at the same time that a current of air was bubbling through the boiler, and as long as the strength of the solution was equal to or above one-one hundred and sixtieth normal no rusting has ever taken place. Since this strength is approximately equivalent to 1 pound of the salt in 1,500 gallons of water, there seems to be no reason why potassium bichromate should not come into use as a boiler protective. The application of the various inhibitors in the priming coats of paints and other protective coverings has already been to some extent made use of, and it would appear that slightly soluble chromates should be theoretically the best protectives for the first application to iron and steel surfaces.

A very widespread impression prevails that charcoal iron and puddled wrought iron are more resistant to corrosion than steel manufactured by the Bessemer and open-hearth processes. It is by no means certain that this is invariably the case, but it would follow from the electrolytic theory that in order to have the highest resistance to corrosion a metal should either be as free as possible from certain impurities, such as manganese, or should be so homogeneous as not to retain localized positive and negative nodes for a long time without change. Under the first condition the irons would seem to have the advantage, but under the second much would depend upon care exercised in manufacture, whatever process was used.

The evidence appears to be conclusive that the corrosion of iron in all its forms is primarily due to hydrogen ions. The ability of various samples to resist the attack of an acid of a standard strength may turn out to bear some relation to resistance to corrosion under service conditions. A great variation in resistance to acid corrosion is shown by different specimens of both iron and steel. An investigation of this subject is being made in connection with the work of Committee U of the American Society for Testing Materials. Carelessly made and poorly segregated metal will be easily attacked, no matter what it

may be called or what method was used in its manufacture. As has already been pointed out, there are two lines of advance by which we may hope to meet the difficulties attendant upon rapid corrosion. One is by the manufacture of better metal, and the other is by the use of inhibitors and protective coverings. Although it is true that laboratory tests are frequently unsuccessful in imitating the conditions in service, it nevertheless appears that chromic acid and its salts should under certain circumstances come into use to inhibit extremely rapid corrosion by electrolysis.

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